Inorganic arsenic - SPE HG-AAS method for RICE tested in-house and collaboratively

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INORGANIC ARSENIC

SPE HG-AAS RICE METHOD TESTED IN-HOUSE AND COLLABORATIVELY

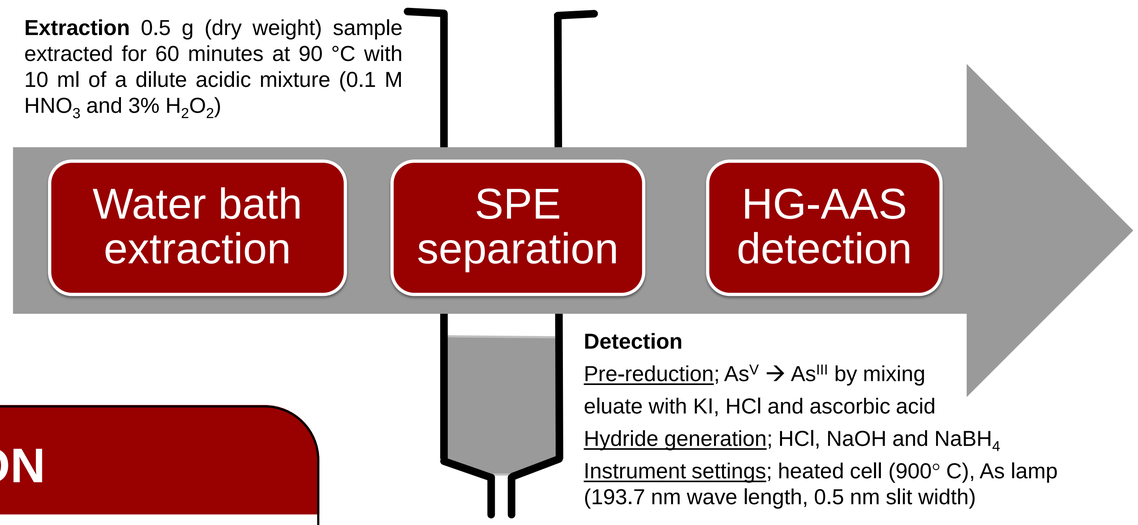
INTRODUCTION

Internationally accepted validated method(s) are needed for establishment of a maximum level (ML) for inorganic arsenic (iAs) in rice as recently emphasised by the European Food Safety Authority (2009), the World Health Organization (2011) and Codex Alimentarius (2012).

Rice contains most often three forms of the trace element arsenic; iAs and the methylated species monomethylarsonic acid (MA^V) and dimethylarsinic acid (DMA^V). Dietary intake of iAs is of special concern due to its carcinogenicity to humans, whereas DMA and MA are generally considered of less toxicological importance.

CONCLUSION

This SPE HG-AAS method enables selective determination of inorganic arsenic in rice and rice products by use of inexpensive instrumentation (HG-AAS) and is a **candidate method for future control**.



SPE SEPARATION

- **The charge of the arsenic species depends on pH**
- pH 5-7 → iAs^V is negatively charged
- SPE → strong anion exchange
- Sequential elution:

1. Pre-condition of SPE, MeOH
2. Equilibrate SPE, 35 mM $(NH4)_2CO_3$, 0.05 M HNO_3, 1.5% H_2O_2
3. Load buffered sample: pH 5.0-7.5
4. Wash SPE, 0.5 M CH_3COOH
5. Elute SPE, 0.4 M HNO_3

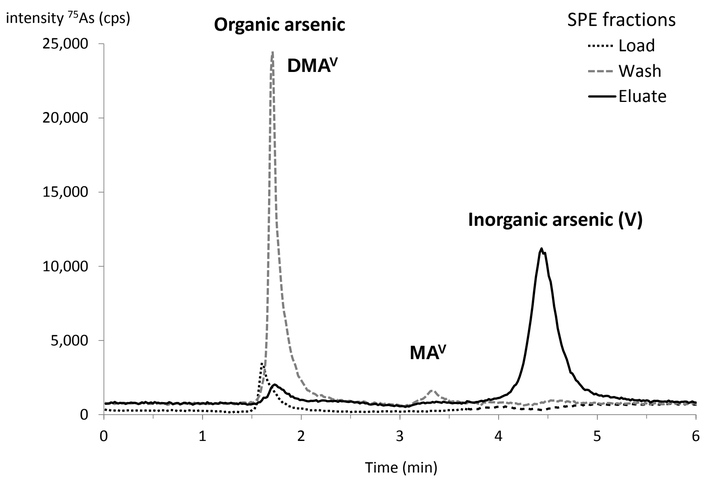


Figure 1. Overlaid HPLC-ICP-MS chromatogram of 3 SPE fractions (load, wash and eluate) of a rice sample (NIST1568a) containing both inorganic and organoarsenic species.

SPE HG-AAS vs HPLC-ICP-MS

A comparison of the results from the two methods (Fig. 3) showed good agreement.

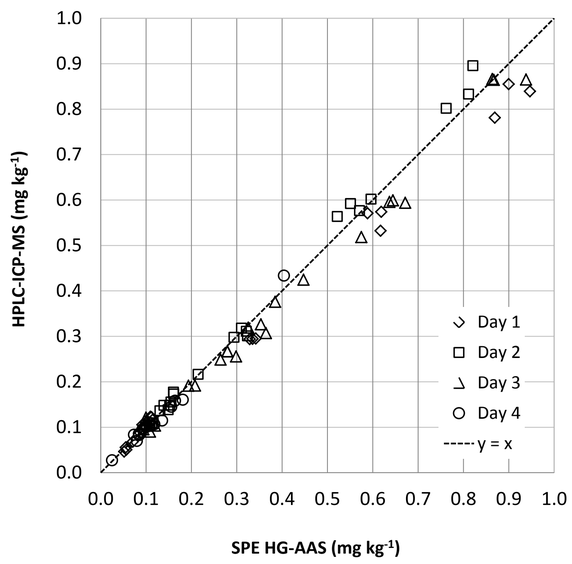


Figure 3. Determination of inorganic arsenic by two different methods; HPLC-ICP-MS and SPE HG-AAS. In total results for 84 spiked and natural incurred rice samples analysed on four different days. The correlation is y=x (99% confidence interval - regression analysis by Excel 2010).

VALIDATION RESULTS

In-house validation was satisfying (Tab 1.) and was in accordance with previous results for marine samples (Rasmussen et. al 2013). The LOD (0.02 mg·kg^{-1}) was below the proposed maximum levels (0.2-0.3 mg·kg^{-1}).

Table 1. In-house validation

	Spiked rice samples			Rice reference materials	
	Low	Medium	High	IMEP-107	NIST1568a
Target level (mg·kg^{-1})	0.30	0.55	0.80	0.107*	0.096*
Observations (N)	9	9	9	8	7**
Mean recovery (%)	105	106	106	101	103
Repeatability RSD_{ir} (%)	5	3	4	6	5
Reproducibility RSD_{IR} (%)	7	9	8	7	7

*) Consensus mean values: IMEP-107 (de la Calle MB et al., 2011 TrAC 30:641–651) and NIST1568a (Raab A et al., 2009 J Environ Monit 11:41–44).
**) One outlier result discarded (0.048 mg·kg^{-1}).

Collaborative test of the SPE separation method on a wholemeal rice meal sample gave a satisfactory HorRat value of 1.6 **among 10 laboratories**.

RICE SAMPLES

The iAs concentration determined by SPE HG-AAS in 36 rice samples purchased on the Danish retail market varied (**0.03–0.60 mg·kg^{-1}**), with the highest concentration found in a red rice sample.

DTU Food
National Food Institute

References
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